PB85-231892

Removal of Azo Dyes by the Activated Sludge Process

(U.S.) Environmental Protection Agency
Cincinnati, OH

Jul 85

U.S. Department of Commerce
National Technical Information
NTIS

PB85-231892

EPA/600/D-85/145
July 1985

REMOVAL OF AZO DYES BY THE ACTIVATED SLUDGE PROCESS

by

Glenn M. Shaul
Clyde R. Dempsey
and
Kenneth A. Dostal

INDUSTRIAL WASTES AND TOXICS TECHNOLOGY DIVISION
WATER ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

WATER ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/D-85/145		PB85 231892/AS

4. TITLE AND SUBTITLE	5. REPORT DATE
Removal of Azo Dyes by the Activated Sludge Process	July 1985
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Glenn M. Shaul, Clyde R. Dempsey, Kenneth A. Dostal	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Industrial Wastes and Toxics Technology Division Water Engineering Research Laboratory U.S. Environmental Protection Agency Cincinnati, Ohio 45268	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Industrial Wastes and Toxics Technology Division Water Engineering Research Laboratory U.S. Environmental Protection Agency Cincinnati, Ohio 45268	Research 10/84 - 5/85
	14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES

Contact: Glenn M. Shaul (513) 684-2621

16. ABSTRACT

The Water Engineering Research Laboratory, Office of Research & Development, U.S. Environmental Ptoection Agency (EPA) is conducting research designed to develop techniques for predicting the fate of azo dyes in typical wastewater treatment systems which are treating wastewater contaminated with azo dyes. These techniques are being developed for EPA Office of Toxic Substance's use in the Premanufacture Notification (PMN) review process under section 5 of the Toxic Substances Control Act (TSCA) and potentially in the regulation of hazardous chemical substances and mixtures under TSCA section 6. A part of this research involves pilot plant investigations on the removal of azo dyes by the activated sludge process. Azo dyes are of concern to OTS because some of the dyes, dye precursors or their degradation products have been shown to be, or are suspected to be, carcinogenic. Therefore, the principal objectives of this research project will be to determine the fate of the dye compounds in the activated sludge treatment process.

The results from this research are needed by OTS to aid in predicting the degree to which new azo dyes and/or their degradation products pass through the activated sludge process. This research will, hopefully, lead to the development of a predictive model of dye compound behavior based upon chemical structure, physical properties and/or dye classification.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Azo Dyes Activated Sludge Adsorption	Biological Treatment	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	19
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U. S. Environmental Protection Agency policy and approved for public distribution and/or publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

REMOVAL OF AZO DYES
BY THE ACTIVATED SLUDGE PROCESS

INTRODUCTION

The Water Engineering Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency (EPA) is conducting research designed to develop techniques for predicting the fate of azo dyes in typical wastewater treatment systems which are treating wastewater contaminated with azo dyes. These techniques are being developed for EPA Office of Toxic Substance's use in the Premanufacture Notification (PMN) review process under section 5 of the Toxic Substances Control Act (TSCA) and potentially in the regulation of hazardous chemical substances and mixtures under TSCA section 6. A part of this research involves pilot plant investigations on the removal of azo dyes by the activated sludge process. Generally, azo dyes contain between one and four azo linkages (-N = N-), linking phenyl and naphthyl radicals that are usually substituted with some combination of functional groups including: amino ($-NH_2$); chloro (-Cl); hydroxy (-OH); methyl ($-CH_3$); nitro ($-NO_2$) and sulfonic acid, sodium salt ($-SO_3Na$). Azo dyes are of concern to OTS because some of the dyes, dye precursors or their degradation products such as aromatic amines, which are also dye precursors, have been shown to be, or are suspected to be, carcinogenic (1). Therefore, the principal objective of this research project will be to determine the fate of the dye compounds in the activated sludge treatment process.

The results from this research are needed by OTS to aid in predicting the degree to which new azo dyes and/or their degradation products pass through the activated sludge process. This research will, hopefully, lead to the development of a predictive model of dye compound behavior based upon chemical structure, physical properties and/or dye classification. This report presents

background information and results to date (5/85) for this ongoing project which is being performed at the EPA's Test and Evaluation Facility in Cincinnati, Ohio.

LITERATURE REVIEW

Limited work on aerobic biological treatment systems has been done regarding the fate of specific dye compounds in industrial or industrial/municipal wastewaters. Most of the research on aerobic systems has utilized synthetic wastewater which allows use of simplified analytical methodology but this does not represent the variability inherent in actual wastewaters. However, much of what has been done is still useful in predicting the fate of specific compounds in these treatment systems.

Straley (2) in his review of the literature stated that,"...dyes are generally recalcitrant to biodegradation since one of the important factors in selecting a dye is its resistance to oxidation." Some researchers (3,4,5) have shown that azo dyes can be slowly biodegraded. However, the primary removal mechanism of dyes from wastewater treated by activated sludge seems to be adsorption onto biological sludge solids (6). Hitz, et al (7) reported that adsorption of dyes depends on the class of dye and the structural differences within the classes. Hitz made the following general conclusions based on limited aerobic jar tests with biological solids:

Acid dyes: poorly adsorbed, dependent on the number of SO_3H groups

Reactive dyes: very little adsorption

Direct dyes: high adsorption

Disperse dyes: high to medium adsorption

Basic dyes: high adsorption.

Tincher (8) studied the removal of acid and disperse dyes (although not all dyes were of the azo type) in a synthetic industrial wastewater simulating a carpet dyeing process wastewater. Generally, he found wide fluctuations in removal of these dyes and speculated that when removal did occur the removal mechanism was probably adsorption onto sludge rather than biodegradation. He concluded that carbon adsorption in conjunction with biological treatment appeared to be a particularly effective treatment system for the removal of dyes from wastewaters.

Wuhrmann, et al. (9) stated that permeation of dyes through the cell membrane is the primordial rate limiting step in the microbial decolorization of azo dyes and sulfonic acid substitution (causing increased water solubility) seems to be an effective inhibitor of permeation.

BACKGROUND

No "standard analytical methods" for specific dye compounds in wastewater and sludge samples exist (10,11). However, Tincher (8) and Dickson (12) have developed an analytical method. Based upon their data, it was decided that the methodology seemed to be appropriate for the liquid samples from an activated sludge process and may be applicable on the sludge samples.

Since it was desirous to spike the dyes into actual wastewaters, it was important that realistic dosages be selected. Discussions with OTS representatives from a trade association, the Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry resulted in selection of dosages for combined industrial/municipal wastewaters (1-5 mg/l) and industrial wastewaters (3-15 mg/l).

OTS initially identified the following dyes to be studied listed by official Colour Index (C.I.) name and number (13):

Name	Number	Name	Number
C.I. Acid Yellow 151	13906	C.I. Acid Brown 14	20195
C.I. Acid Orange 7	15510	C.I. Acid Black 1	20470
C.I. Acid Red 1	18050	C.I. Acid Black 52	15711
C.I. Acid Red 88	15620	C.I. Disperse Yellow 23	26070
C.I. Acid Red 151	26900	C.I. Disperse Orange 25	11227
C.I. Acid Red 337	-	C.I. Disperse Red 1	11110
C.I. Acid Blue 113	26360	C.I. Disperse Blue 79	-

These dyes were selected for one or more of the following reasons:

- Chemical structure is similar to dyes being submitted to EPA for PMN review;
- Analytical methods for the possible detection of the dyes in wastewater samples had been developed (8);
- Current high production volumes;
- Commercial dye compounds are readily available and chemical structure is known.

The pilot plant systems used for this study, described in detail in a previous paper (14), are continuous flow, completely mixed, activated sludge treatment systems made of acrylic material with 40 liter primary and secondary clarifers and 200 liter aeration basins.

EXPERIMENTAL PROGRAM

This paper describes initial work with an industrial/municipal wastewater. The source of this influent wastewater was from the Greater Cincinnati

Metropolitan Sewer District, Mill Creek Sewage Treatment Plant. Table 1 shows the operating conditions of the pilot plants and Table 2 presents a summary of the mean raw wastewater characteristics from August 1984 to March 1985.

TABLE 1. SUMMARY OF OPERATING CONDITIONS

Parameter	Value
Influent Flow Rate, L/d	720
Primary Sludge Flow Rate, L/d	6
Primary Effluent Flow Rate, L/d	714
Mixed-Liquor Wastage Flow Rate, L/d	67
Secondary Effluent Flow Rate, L/d	647
Solids Retention Time, days	2.7
Hydraulic Retention Time, days	0.28
Dissolved Oxygen, mg/L	2.0-3.0
Influent Spike Dosages, mg/L	
Low	1
High	5
Influent pH, pH units	7.0-8.0
Aeration Basin Temperature, °C	25

TABLE 2. RAW WASTEWATER CHARACTERISTICS

Parameter	Mean Value
Biochemical Oxygen Demand, BOD_5	220 mg/L
Chemical Oxygen Demand, COD	400 mg/L
Total Suspended Solids, TSS	290 mg/L
Total Kjeldahl Nitrogen, TKN	30 mg/L as N
Total Phosphorus	6 mg/L as P
pH	7.0 - 8.0 pH units

All systems were operated for at least three times the solids retention time (SRT) to ensure acclimation prior to initiation of data collection. During the intensive data collection period, the following analytical tests were performed:

- Total and volatile suspended solids (TSS and VSS) analyses on the influent (INF), primary effluent (PE), mixed liquor (ML) and activated sludge secondary effluent (ASE) samples;
- Specific dye analyses on the INF, PE and ASE samples.

All samples were 24-hour composites made up of six grab samples collected every four hours and stored at 4°C. All TSS and VSS analyses were conducted using EPA approved methods (10). Each test run was sufficiently long to allow at least six sets of samples (after acclimation) for the specific dye analyses. If acclimation appeared to be continuing during the data collection phase, the intensive data collection period was extended accordingly.

PRELIMINARY ANALYTICAL INVESTIGATIONS

As previously discussed, the methodology developed by Tincher (8) and Dickson (12) was employed for this study although it had to be modified. Quantitative recovery of a water soluble dye from a wastewater sample is a difficult job. It has been reported (8) that resins such as XAD-2 will preferentially adsorb organic compounds like azo dyes and this property was employed for azo dye determination. As adapted for this project, the steps in the analysis were: preparation of standards, adsorption of the dye onto XAD-2 resin, solvent extraction of the adsorbed dye, solvent evaporation, and high performance liquid chromatography (HPLC) analysis with UV-visible detection.

The method utilizes an adsorption column filled with about 30 ml of XAD-2 resin slurried in methanol. The column is first downwashed with water and then backwashed to ensure uniform distribution of the resin within the column. A wastewater sample is filtered to remove suspended solids and the filtrate as well as the filter paper and residue are saved. A reservoir containing a filtered sample is attached to the top of the column and the sample is passed through the column at a rate of about 3 ml/min. The slow percolation rate is necessary to ensure that all of the dye is adsorbed on the resin. This part of the procedure takes about eight hours to complete. The recovered dye and resin and the filter paper and residue are then transferred to an extraction thimble and extracted with pyridine for a period of six hours. The dye and solvent are transferred to a rotary evaporator and the solvent removed until the sample is dry. The residue is redissolved in an appropriate solvent system and diluted to 50 ml. Then a sample is taken and injected into the HPLC and quantified by comparing the dye sample with a series of standards of known concentration.

An acceptable percent recovery range of laboratory spikes was set at 80-120% although deviations from this range could be used if the recoveries were consistent. Prior to all intensive sampling periods, recovery studies utilizing organic free water and various liquid samples from the treatment system were performed in order to assess the spike recoveries from these matrices. In addition, dye recovery from sludge studies was performed during the preliminary analytical investigations and the results were variable with generally less than 30% recovery. As a result, sludge samples were not collected during the intensive sampling periods. Investigations on improved recovery of dye from samples containing large amounts of suspended solids continue.

RESULTS AND DISCUSSIONS

Table 3 presents the mean flows and mean concentrations and standard deviations of the influent, primary effluent and secondary effluent samples from six data sets for C.I. Acid Red 88 and total suspended solids (TSS) (mixed liquor data included). As can be seen from the mean influent values, the targeted spike dosages for the parallel biological systems of 1 mg/L (low) and 5 mg/L (high) were achieved. An inspection of the data indicates that primary clarification removed about 20% of the dye compound while the activated sludge process removed about 90% of the remaining dye compound. Effluent suspended solids values were monitored to determine if any adverse effect from the dye on the treatment systems occurred. If the values were consistently less than 30 mg/L, it was assumed that no negative impact occurred.

TABLE 3. C.I. ACID RED 88 DATA*

	Influent			Primary Effluent			Primary Sludge	Waste Activated Sludge		Secondary Effluent		
	Q_1	SS_1	D_1	Q_2	SS_2	D_2	Q_4	Q_5	SS_5	Q_3	SS_3	D_3
						Low Dye Spike						
Mean	720	253	1.06	714	125	0.85	6	67	1680	647	8	0.10
Std. Dev.		60	0.20		29	0.20			210		6	0.04
						High Dye Spike						
Mean	720	253	4.94	714	135	3.88	6	67	1630	647	13	0.42
Std. Dev.		35	1.16		58	0.57			201		6	0.32

*Units: Q = Flow, L/day
SS = Total Suspended Solids, mg/L
D = Total Dye Concentration, mg/L

The possible removal mechanisms for a dye compound in the activated sludge treatment system include adsorption, biodegradation, chemical transformation, photodegradation and air stripping. During the spike recovery studies several influent and effluent samples from the treatment systems were spiked with dye standards and overall recovery from eight samples was 91 $\pm$ 17%. As a result of these tests, it appeared that little or no chemical transformation of C.I. Acid Red 88 occurred due to contact with the variable wastewater matrix. In addition, photodegradation potential was investigated with dye added to distilled/deionized water and no measurable decrease in concentration was observed for samples held in the light for more than 30 days. Moreover, the estimated Henry's Law constant for C.I. Acid Red 88 is 10^{-18} (dimensionless) and as such, air stripping is very unlikely (15). Therefore, adsorption and/or biodegradation appeared to be possible removal mechanisms.

Assuming there is no biodegradation of the dye an estimate of the amount of dye adsorbed on the suspended solids in the aeration basin can be made based upon mass balance calculations. Figure 1 presents a schematic of the treatment system with flow rates in L/d (Q), suspended solids concentrations in mg/L (SS), total dye concentrations in mg/L (D), estimated soluble dye concentration in mg/L (C) and estimated dye concentration on the suspended solids in mg/mg (X). The subscripts are used to denote the process flow streams: influent (1), primary effluent (2), secondary effluent (3), primary sludge (4) and waste activated sludge (5).

Initial mass balance assumptions are outlined below.

- the dye removed by the suspended solids is due to adsorption;
- no stripping, biodegradation, photodegradation, or transformation of the dye compound occurs;

- since the aeration basin is completely mixed these equalities hold:

  $C_3 = C_5$, and $X_3 = X_5$.

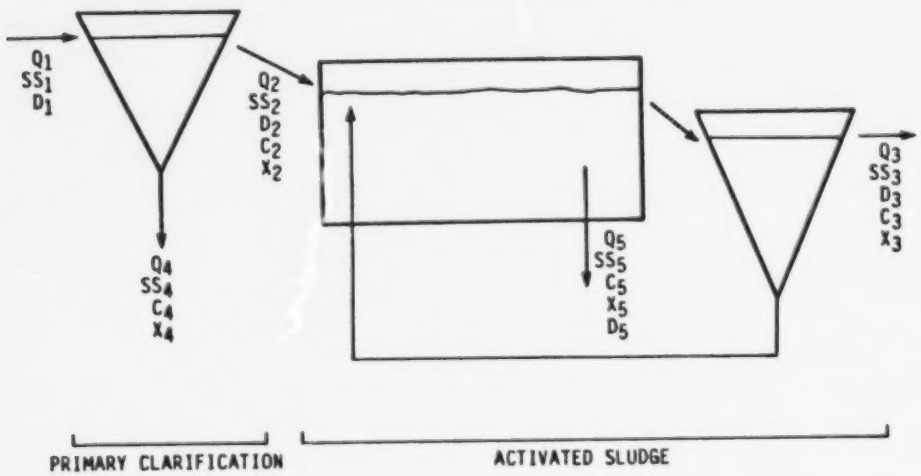

Figure 1. Process Schematic

For both the secondary effluent and the waste activated sludge streams an equation can be written to describe the relationship between C and X.

For the secondary effluent:

$$Q_3 D_3 = Q_3 C_3 + Q_3 (SS_3) X_3$$

$$\text{or} \quad D_3 = C_3 + X_3 (SS_3) \qquad (1)$$

For the waste activated sludge:

$$Q_5 D_5 = Q_5 C_5 + Q_5 X_5 (SS_5) \qquad (2)$$

and $Q_2 D_2 = Q_3 D_3 + Q_5 D_5$ or $Q_5 D_5 = Q_2 D_2 - Q_3 D_3$ (3)

$\therefore Q_2 D_2 - Q_3 D_3 = Q_5 C_5 + Q_5 X_5 (SS_5)$

since $C_5 = C_3$, $X_5 = X_3$

Then $Q_2 D_2 - Q_3 D_3 = Q_5 C_3 + Q_5 X_3 (SS_5)$

From (1) $C_3 = D_3 - X_3 (SS_3)$

Then $Q_2 D_2 - Q_3 D_3 = Q_5 [D_3 - X_3 (SS_3)] + Q_5 X_3 (SS_5)$

$Q_2 D_2 - Q_3 D_3 - Q_5 D_3 = X_3 [Q_5 (SS_5) - Q_5 (SS_3)]$

$Q_2 D_2 - D_3 (Q_3 + Q_5) = Q_5 X_3 [(SS_5) - (SS_3)]$

$Q_3 + Q_5 = Q_2$ (4)

$Q_2 D_2 - Q_2 D_3 = X_3 Q_5 [(SS_5) - (SS_3)]$

$$\frac{Q_2 (D_2 - D_3)}{Q_5 [(SS_5)-(SS_3)]} = X_3 \quad (5)$$

From (1) $C_3 = D_3 - X_3 (SS_3)$ (6)

Using the data from Table 3 and equations (5) and (6) allows the calculation of X_3 and C_3:

$C_3 = C_5 = 0.062$ mg/L
$X_3 = X_5 = 0.0048$ mg/mg — Low Spike

$C_3 = C_5 = 0.121$ mg/L
$X_3 = X_5 = 0.023$ mg/mg — High Spike

Although the primary clarifier was not a completely-mixed system similar calculations for C and X were made assuming $C_2 = C_4$ and $X_2 = X_4$.

The mass balances equations simplified to

$$X_2 = \frac{D_1 - D_2}{SS_1 - SS_2} \quad (7)$$

and $C_2 = D_2 - (SS_2)X_2$ (8)

The results were:

$C_2 = C_4 = 0.65$ mg/L
$X_2 = X_4 = 0.0016$ mg/mg — Low Spike

$C_2 = C_4 = 2.66$ mg/L
$X_2 = X_4 = 0.0090$ mg/mg — High Spike

An estimate of the amount of dye adsorbed onto the mixed-liquor suspended solids can also be determined via adsorption isotherm tests. Lieberman, et al[16] determined the adsorption isotherm for C.I. Acid Red 88 onto inactivated, activated sludge solids (inactivation process: lyophilization followed by heating at 103°C) and Figure 2 presents the data. The equation of the line was estimated to be $Y/M = (3.9)\ C_e^{0.64}$ where Y/M is the mass of dye removed per mass of suspended solids (mg/g) and Ce is the remaining concentration (mg/L of dye in solution.

Also shown on Figure 2 are the four sets of C and X values calculated above. Although the isotherm was generated using inactivated biological solids, not primary sludge solids, it is interesting to note that the partitioning of the dye in the primary effluent and sludge was similar to that predicted by the isotherm.

As shown on the Figure the apparent dye loadings on the active biological solids were significantly higher than predicted by the isotherm. This led to the conclusion that biological degradation accounted for much of the measured removal by the activated sludge process. Therefore, the mass balance equations were modified in order to estimate the amount of dye that was degraded. An additional assumption was made: the dye loadings on the biological solids in the waste sludge and in the final effluent could be predicted from the equation of the isotherm $Y/M = (3.9)\ C_e^{0.64}$

Equation (6) can be solved for C_3 by substituting $X_3 = \frac{3.9}{1000} C_3^{0.64}$ and then X_3 can be calculated. The results are:

C_3 = 0.094 mg/L

Low Spike

X_3 = 0.00075 mg/mg

C_3 = 0.39 mg/L

High Spike

X_3 = 0.0020 mg/mg

Using these values and the data in Table 3, calculations of the amount of dye that is adsorbed and the amount that is apparently biodegraded is straightforward. The results are shown in Table 4. Biodegradation was estimated to account for 74-81% of the removal across the secondary system.

Since a substantial amount of C.I. Acid Red 88 appeared to be biodegradable, the specific substrate utilization rate, K, can be estimated using the substrate limiting form of the equation.

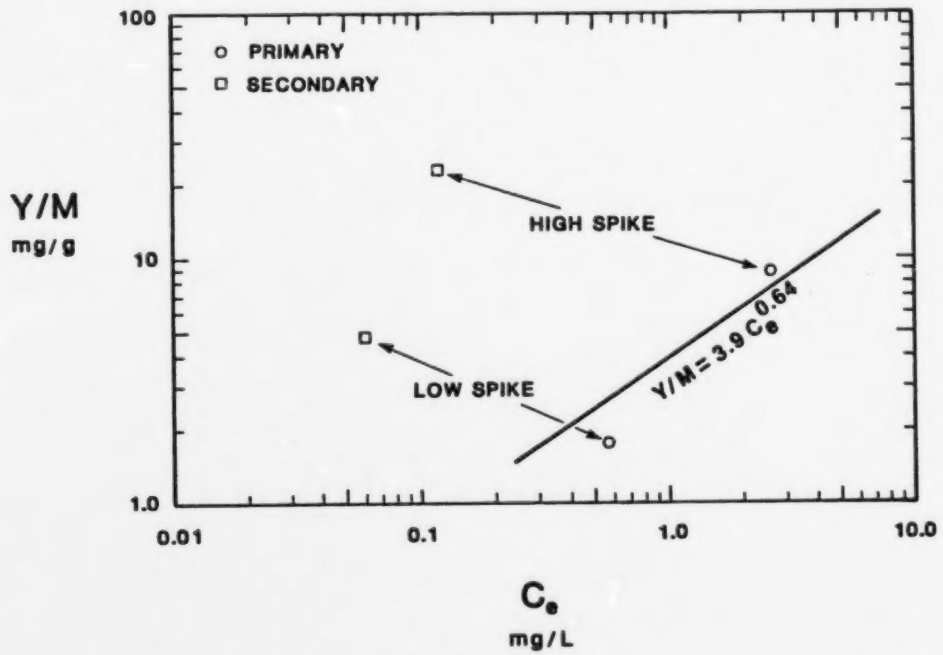

Figure 2. C.I. Acid Red 88 Adsorption Isotherm

TABLE 4. C.I. ACID RED 88 ESTIMATED PERCENT REMOVALS BY ACTIVATED SLUDGE PROCESS

	Adsorption Only	Biodegradation Only	Total
Low Spike	15	74	89
High Spike	9	81	90

$$S_eK = \frac{S_o - S_e}{(MLSS)t} \quad (4)$$

where: K = specific substrate utilization rate, $days^{-1}$

S_o = influent dye concentration, mg/L

S_e = effluent soluble dye concentration, mg/L

MLSS = mixed liquor TSS, mg/L

t = hydraulic retention time, days

The calculated values of K using the estimated soluble values (C_3) for S_e were 0.019 $days^{-1}$ for the low spike system and 0.021 $days^{-1}$ for the high spike system.

STATUS

No overall prediction about the fate of azo dyes in conventional activated sludge systems can be made at this time as previously indicated. Several additional compounds need to be tested before generalities can be attempted. However, all test data will be analyzed as outlined in this report. It is hoped that improved dye recovery from sludge can be achieved so that much of the estimation in the mass balance calculations can be minimized. And, as previously stated, if biodegradation appears to be a major removal mechanism, attempts will be made to identify degradation products.

CONCLUSIONS

- Based upon the data and assumptions outlined, biological degradation appeared to be a significant removal mechanism for C.I. Acid Red 88.

- C.I. Acid Red 88 was also removed by adsorption.

REFERENCES

1. Helmes, C.T., et al, "A Study of Azo and Nitro Dyes for the Selection of Candidates for Carcinogen Bioassay," Journal of Environmental Science and Health, Volume A19, No. 2, 97-231 (1984).

2. Straley, J. P., "Selected Bacterial Cultures for Textile Wastewaters" in American Dyestuff Reporter, Sept. and Oct., 1984.

3. Kulla, H. G., "Aerobic Bacterial Degradation of Azo Dyes," in Microbial Degradation of Xenobiotics and Recalcitrant Compounds, Academic Press, Inc., London (1981).

4. Pratt, H. D., "A Study of the Degradation of Some Azo Disperse Dyes in Waste Disposal Systems," M. S. Thesis, Georgia Institute of Technology, (1968).

5. Anliker, R., Clarke, E. A. and Moser, P., "Use of the Partition Coefficient as an Indicator of Bioaccumulation Tendency of Dyestuffs in Fish," Chemosphere, Vol. 10, No. 3, pp. 263-274 (1981).

6. Dohanyos, M., Madera, V. and Sedlacek, M., "Removal of Organic Dyes by Activated Sludge," Progress in Water Technology, Vol. 10, Nos. 5/6, pp. 559-575, Pergamon Press (1978).

7. Hitz, H. R., et al., "The Adsorption of Dyes on Activated Sludge," Journal of the Society of Dyers and Colorists, 94, pp. 71-76 (Feb., 1978).

8. Tincher, W. C., "Survey of the Coosa Basin for Organic Contaminants from Carpet Processing," Contract No. 3-27-630 for the Environmental Protection Division, Department of Natural Resources, State of Georgia (1978).

9. Wuhrmann, K., Mechsner, Kl., and Kappeler, Th., "Investigation on Rate-Determining Factors in the Microbial Reduction of Azo Dyes," European Journal Applied Microbiology and Biotechnology, 9, pp. 325-338 (1980).

10. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, Environmental Monitoring and Support Laboratory, U. S. EPA (1979).

11. "Standard Methods for the Examination of Water and Wastewater," 15th ed. (Washington, DC: American Public Health Association, 1980).

12. Dickson, D. N., "The Effectiveness of Biodegradation in the Removal of Acid Dyes and Toxicity from Carpet Dyeing Wastewater," M. S. Thesis, Georgia Institute of Technology (1981).

13. Colour Index, Revised 3rd Edition, Six Volumes, published by The Society of Dyers and Colourists (1975).

14. Shaul, G. M., Barnett, M. W. and Dostal, K. A. "Treatment of Dyes and Pigments Processing Wastewater by the Activated Sludge Process," in Proceedings of the 37th Purdue Industrial Waste Conference, Purdue University (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1982).

15. Lyman, W., Reehl, W. and Rosenblatt, D., Handbook of Chemical Property Estimation Methods, McGraw Hill Book Company, New York: 1982.

16. Lieberman, R. J., Shaul, G. M. and Dostal, K. A., "An Evaluation of Adsorption Isotherms for Azo Dyes," in Proceedings of the 40th Purdue Industrial Waste Conference, Purdue University (1985).